LOW COST COAL-BASED CARBONS FOR COMBINED SO_2 AND NO REMOVAL FROM EXHAUST GAS.

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ABSTRACT

The aim of this paper is to show how a cheap carbonaceous material such as low rank coal-based carbon (or char) can be used in the combined SO_2/NO removal from exhaust gas at the linear gas velocity used in commercial systems (0.12 m s^{-1}). Char is produced from carbonization and optionally activated with steam. This char is used in a first step to abate the SO_2 concentration at the following conditions: 100ºC, space velocity of 3600 h^{-1}, 6% O_2, 10% H_2O, 1000 ppmv SO_2, 1000 ppmv NO and N_2 as remainder. In a second step, when the SO_2 concentration in the flue gas is low, NO is reduced to N_2 and steam at the following experimental conditions: 150ºC, space velocity of 900 h^{-1}, 6% O_2, 10% H_2O, 0-500 ppmv SO_2, 1000 ppmv NO, 1000 ppmv NH_3 and N_2 as remainder.

It has been shown that the presence of NO has no effect on SO_2 abatement during the first step of combined SO_2/NO removal system and that low SO_2 inlet concentration has a negligible effect on NO reduction in the second step. Moreover, this char can be thermally regenerated after use for various cycles without loss of activity. On the other hand, this regenerated char shows the highest NO removal activity (compared to parent chars, either carbonized or steam activated) which can be attributed to the activating effect of the sulfuric acid formed during the first step of the combined SO_2/NO removal system.

KEYWORDS: coal-based carbon, flue gas cleaning, combined SO_2/NO removal.

INTRODUCTION

Sulfur and nitrogen oxides are important air pollutants that cause photochemical smog and acid rain. This knowledge has led to increasing regulation of exhaust emissions from stationary combustion sources.

It has been shown in the literature that activated carbon and active coke act simultaneously as adsorbent and as catalyst at low temperatures [1-5]. SO_2 becomes adsorbed on carbonaceous materials and is catalyzed by the carbonaceous surface and converted to sulfuric acid. The same carbonaceous material catalyzes the reaction of NO with NH_3 to N_2 and steam. This is the basis for processes for combined SO_2 and NO removal. However SO_2 adsorption and catalytic NO reduction with ammonia injection do not take place independently. In the temperature range between 100 and 160ºC, the sulfuric acid adsorbed reacts with ammonia producing salts that deactivate the catalyst for NO reduction.

Both targets can be achieved with a two stage SO_2 and NO removal system. In the first stage most of the sulfur dioxide is removed. In this stage the NO concentration is not reduced substantially (~ 5%). Upstream, the second stage, with a decreased SO_2 concentration, ammonia is added principally for catalytic reduction of nitrogen oxides. This is the basis of the process developed by DMT (formerly Bergbau Forschung). Modifications of this process have been carried out by Mitsui Mining and by RTI. The advantages of this system, apart from the combined SO_2 and NO removal, are: a) no requirement for process water and wastewater treatment, b) no need for flue gas re-heating (as with selective catalytic reduction technique based on vanadium-titanium-catalysts) and c) saleable by-product such as elemental sulfur or sulfuric acid. The main disadvantage of this process is the cost of the carbon used, activated coke from bituminous coal. Research on the use of cheap carbonaceous materials with similar properties than activated carbons

is the recent trend [6-9]. In this context, a low rank coal char is evaluated for combined SO_2 and NO removal. In previous papers [10-11] we had studied the influence of the space velocity of gas, the temperature of reaction and the composition of gas on the SO_2 and NO removal performance separately. In the present paper, the influence of NO in the SO_2 abatement and the negative effect of SO_2 during NO reduction by NH_3 is studied. The possibility of thermal regeneration of the used chars and re-use of them is screened as well. The novelty of this contribution is on one hand the use of low-cost carbons for combined SO_2 and NO removal and on the other hand the use of enhanced-regenerated carbons for NO removal in the second step.

EXPERIMENTAL

Materials

A lignite from NE of Spain with high sulfur and ash content (7.0 and 26.8%, respectively) was carbonized in nitrogen atmosphere at 800ºC in an experimental installation described elsewhere [12]. This sample was labeled SC800.

Steam activation was carried out at 700ºC of temperature in a flow of 750 l h^{-1} of steam during 4 hours in an experimental installation described elsewhere [13], obtaining a sample labeled as SC800A (burn-off degree 28%).

These samples were characterized by elemental and proximate analysis, determining the oxygen content directly onto demineralized samples.

The textural characterization of the samples studied was carried out by adsorption of N_2 and CO_2 at -196 and 0ºC, respectively. The outgassing conditions prior the performance of the isotherm were a temperature of 300ºC and a vacuum of 10^{-3} mm Hg.

SO_2 and NO removal capacity test

The SO_2 and NO removal capacity of the samples were tested in an experimental

installation built up for this purpose. It is provided of a system for mixing gases to obtain flue gas composition, a fixed bed reactor (3/4 inch o.d. stainless steel pipe, Swagelock fittings) heated by a furnace and an on-line gas analysis, the effluent concentration of SO_2, NO, O_2, CO and CO_2 being continuously monitored during a experiment. Water vapor was introduced by a flow of saturated nitrogen at a fixed temperature. The experimental installation is provided with a bypass to allow the gas concentration to be measured before introducing the gas mixture into the reactor. The inlet temperature of the gas mixture to the reactor was controlled and the temperature within the reactor was measured by a thermocouple. More details of the experimental installation are given in [10].

The concentration of NO_2 formed by NO oxidation in the gas phase was determined by difference between NO flow before the entrance to the gas phase mixture line and the NO concentration measured on-line by the analyzer, when the reactor is bypassed.

Experimental conditions to carry out the SO_2 and NO removal capacity tests were: a) in a first step a flow of 2 l min^{-1} containing 1000 ppmv NO (present in some selected experiments), 1000 ppmv SO_2, 6%O_2, 10% water vapor and N_2 as balance is passed through a bed 30 g of carbon at 100ºC; b) in a second step a flow containing a remainder amount of SO_2 (between 80-500 ppmv), 1000 ppmv NO, 6%O_2, 10% water vapor 1500 ppmv NH_3 and N_2 as balance is passed through a bed of either fresh or regenerated (after use in the first step) carbon.

The reaction results are described in terms of SO_2 conversion as $\%SO_2=(SO_{2in}-SO_{2out})100/SO_{2in}$ and NO conversion as $\%NO=(NO_{in}-NO_{out})100/NO_{in}$.

The amount of SO_2 removed expressed in mg SO_2 g^{-1} carbon was calculated by integration of SO_2 conversion versus time curves.

Regeneration

Regeneration of the exhausted carbons was carried out at 400ºC of temperature and a flow

of 0.5 l min^{-1} N_2. Time used for regeneration was variable depending on the evolution of SO_2, considering the final point when the concentration was below 50 ppmv SO_2.

Samples regenerated after fist SO_2 adsorption/regeneration cycle were labeled as SC800R and SC800AR, corresponding to the regeneration of exhausted SC800 or SC800A, respectively.

RESULTS

Table 1 shows the ultimate and proximate of the samples studied in this work. It can be emphasized the high ash content of the samples studied, particularly the activated samples.

Surface area values of the samples measured by N_2 and CO_2 adsorption are given in Table 2 as well as the volume of macro+mesopores and the volume of micropores. The Brunauer- Emmett-Teller (BET) equation was applied to N_2 adsorption isotherms and the Dubinin-Radushkevich (DR) equation to CO_2 adsorption data. The meso and macropore volume values were taken from the Barret-Joyner-Halenda curves (BJH) calculated from N_2 adsorption data. The range of pore size diameters covered by the BHJ calculations was from about 17 to 3000 Å (large micropores and mesopores). The micropore volume values were obtained from CO_2 isotherm.

The surface areas obtained from CO_2 adsorption are always higher than those obtained from N_2 adsorption. In the case of non-activated samples these differences are higher, indicating pore constrictions at the entrance of the micropores. These differences become smaller for activated carbons indicating an opening of the porosity [14, 15].

Regenerated samples show lower surface areas and pore volumes than those corresponding to their parent char (SC800R->SC800 and SC800AR->SC800A).

Figure 1 shows the SO_2 conversion versus time for sample SC800 in absence and in presence of NO. It can be observed that the shape of the breakthrough curve is not modified by the presence of NO in the gas stream. The SO_2 removal capacity measured as the amount of SO_2 removed from the gas stream by gram of sample (given in Figure 2) is quite similar for both type of experiments, that is in absence and in presence of NO.

In the case of activated sample, cycles of SO_2 adsorption/regeneration were carried out in order to evaluate the possibility of thermal regeneration and re-use of these low-rank coal-based carbons. Figure 2 shows the SO_2 removal capacity of sample SC800A in presence of NO for fourteen adsorption/regeneration cycles. As can be seen in this Figure, after each cycle, the SO_2 removal capacity of the sample increases slightly.

The NO removal capacity of the parent samples is low. Only conversions below 45% are obtained in absence of SO_2 in the flue gas, as can be seen in Figure 3 (corresponding to origin points). However, the thermal regenerated samples exhibit a high activity for NO removal in the absence of SO_2 in the gas stream. Both regenerated samples SC800R and SC800AR were chosen to study the effect of the presence of SO_2 in the gas stream on the activity of these carbons for NO removal

The presence of SO_2 in the gas stream negatively affects the NO removal capacity of both samples in presence of ammonia. Experiments changing the concentration of SO_2 in the gas stream were carried out to study this negative effect. Figure 3 shows the NO conversion versus different SO_2 concentrations in the gas stream for the regenerated samples. During these experiments, SO_2 is removed from the gas stream as in the previous type of experiments. It can be observed that at low SO_2 concentrations, NO removal capacity of sample is slightly affected by the presence of SO_2. The increase of SO_2 concentration over different values, depending on the sample, produces an important decrease in NO conversion.

DISCUSSION

The removal of SO_2 over a carbon in the presence of oxygen and water vapor at low temperature involves a series of reactions that leads to the formation of sulfuric acid as the final product. The overall reaction is [2]:

$$SO_2 + ½\ O_2 + H_2O + C \rightarrow C\text{-}H_2SO_4 \quad (1)$$

It implies that SO_2, O_2 and H_2O are all adsorbed on the surface of the carbon in enough close proximity and in the proper steric configuration to react and form H_2SO_4. The shape of the SO_2 breakthrough curve (Figure 1) can be divided into three subsequent phases. Firstly, the adsorption of SO_2, H_2O and O_2 at the internal surface of the carbon, catalytic oxidation of adsorbed SO_2 to sulfuric acid and transport of the generated acid to readily accessible inner pores. During this first phase no breakthrough is observed. The second phase starts with the breakthrough of the curve and no steady state can be reached by the rate of the catalytic oxidation during this second phase. Finally, the storage capacity of the accessible pores for the sulfuric acid is occupied and the SO_2 conversion declines. In this context, the presence of NO in the gas stream alter neither the shape of the SO_2 conversion curve nor the SO_2 removal capacity of the samples studied. During these experiments, NO conversion is negligible (3-4%), indicating that in absence of ammonia no catalytic NO reduction takes place over the carbon at this temperature. In this way, the SO_2 removal capacity of the carbon is not altered by the presence of NO in the flue gas, because there is no competition for adsorption sites.

During thermal regeneration of exhausted samples after their use in SO_2 abatement experiments the sulfuric acid stored on the carbon is removed acting the carbon as a reducer, following the reaction [16]:

$2\ H_2SO_4 + C \rightarrow 2\ SO_2 + CO_2 + 2\ H_2O$ (2)

The gases evolved from this regeneration is a SO_2-rich gas that can be further processed to produce elemental sulfur, liquid SO_2 or sulfuric acid [1, 2].

After this thermal regeneration, the sample can be used again without loss in the SO_2 removal capacity. On the contrary, there is a slight increase in the amount of SO_2 removed in each adsorption/regeneration cycle. This fact can be explained in terms of the reaction (2) that put up with a mild gasification, leading to a pore opening that helps to the H_2SO_4 storage in the next adsorption cycle. Despite of a loss in surface area due to the loss of microporosity, an increase in macro+meso pore volume occur, as can be deduced from Table 2.

In the literature [2, 17], is assumed that the storage capacity for sulfuric acid depends mainly on pore structure of the adsorbent, and it increases with increasing diameter of micropores. In this work, this dependence is confirmed. Activated sample adsorbs more SO_2 than non-activated sample.

The regeneration after the SO_2 adsorption experiments over the activated sample alters the pore structure of the carbon leading to a pore widening with respect to its parent carbon.

In the case of the NO removal by ammonia in absence of SO_2 in the gas stream, no relationship between surface area of chars and NO removal capacity could be found. As an example sample SC800A exhibit the highest surface area (Table 2) but NO conversion is only of 42% (Figure 3). Here the regeneration step after SO_2 removal experiments enhances the NO removal capacity of the samples in a higher extent than the steam activation. The sulfuric acid formed during the SO_2 adsorption produces an activation of the char that is beneficial to the enhancement of the NO removal capacity of the samples studied. Sulfuric acid is used as a treatment to activate carbons in solution [5, 18] to enhance their activity towards NO reduction. In present work, it has been shown that the

regeneration step (gas-phase sulfuric acid) produces this same effect. The change of surface chemical properties has been studied previously [19] in comparison to traditional sulfuric acid treatment.

The negative effect of the presence of SO_2 in the gas stream above a concentration value (Figure 3) on the NO removal capacity of the samples studied can be explained by the formation of ammonium hydrogen sulfate or ammonium sulfate [2] by the reaction between the sulfuric acid that is stored during the experiment and ammonia, following the reactions:

$$H_2SO_4 + NH_3 \rightarrow NH_4HSO_4 \quad (3)$$

$$NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \quad (4)$$

These salts are deposited on the inner surface of the carbons, poisoning the catalytic sites for NO and leading to a decrease in NO conversion. However, when the concentration of SO_2 is low at the entrance of the reactor where NO is going to be removed, the activity of the char can be maintained for a long period of time. The catalytic activity of char SC800AR was maintained at 87% conversion for more than five days without loss of NO removal capacity when a concentration of 80 ppmv SO_2 is present in the gas stream.

CONCLUSIONS

This work has shown that low cost coal chars can be efficiently used as adsorbent and catalyst for the combined SO_2 and NO removal from flue gas in two steps. In the first step, SO_2 is removed from the gas stream reaching conversions of 100 % and the presence NO do not affect the SO_2 removal capacity of the char. In the second step, NO is reduced to N_2 in presence of ammonia. The presence of low SO_2 concentration in the gas stream has no effect on the NO removal capacity of the chars in the second step.

These carbons not only maintain the SO_2 removal capacity for several adsorption/regeneration cycles but also the regeneration involves a sort of activation (gas-phase sulfuric acid) that enhances the NO removal capacity of the chars, so that these chars can be used without treatments and can reach removal values higher than 80%.

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Table 1. Proximate and ultimate analysis of raw carbons.

Constituent analyzed, %	SC800	SC800A	SC800R	SC800AR
Moisture	0.9	2.1	0.7	0.6
Ash	31.9	42.5	32.0	43.0
Volatile matter	4.1	4.6	3.8	4.1
Carbon[a]	62.4	54.0	61.6	53.2
Hydrogen[a]	1.1	0.8	1.0	0.8
Oxygen[b]	4.7	4.8	5.5	6.8
Total sulphur[a]	4.2	3.9	4.3	4.1

a as received basis

b directly determined onto demineralized samples

Table 2. Textural characterization of carbons studied.

	SC800	SC800A	SC800R	SC800AR
S_{N2} (m^2 g^{-1})	80	310	74	267
S_{CO2} (m^2 g^{-1})	381	440	352	312
$V_{macro\text{-}meso}$[a] (cm^3 g^{-1})	0.062	0.220	0.053	0.243
V_{micro}[b] (cm^3 g^{-1})	0.170	0.190	0.158	0.140

a from N_2 isotherm and Barret-Joyner-Halenda

b from CO_2 isotherm and Dubinin-Radushkevich

FIGURE CAPTIONS

Figure 1. SO_2 breakthrough curves for sample SC800. Experimental conditions: 100ºC, flow of 2 l min^{-1} containing 10% H_2O, 6% O_2, 1000 ppmv SO_2 and 1. no NO present in the gas stream; 2. 1000 ppmv NO present in the gas stream.

Figure 2. Amount of SO_2 removed after 10 h of use at the experimental conditions: 100ºC, flow of 2 l min^{-1} containing 10% H_2O, 6% O_2, 1000 ppmv SO_2 by samples SC800 (in absence or presence of 1000 ppmv NO) and SC800A in presence of 1000 ppmv NO and different adsorption/regeneration cycles.

Figure 3. NO conversion at the experimental conditions: 150ºC, flow of 0.5 l min^{-1} containing 10% H_2O, 6% O_2, 1000 ppmv NO, 1000 ppmv NH_3 and different concentrations of SO_2. ▼ SC800AR; ● SC800R; ▲ SC800A; ■ SC800.

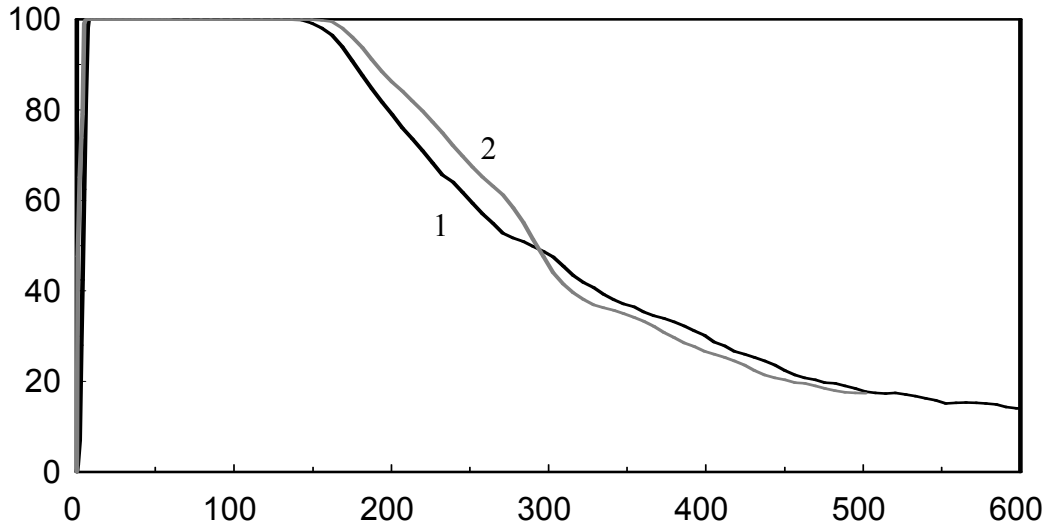

Figure 1

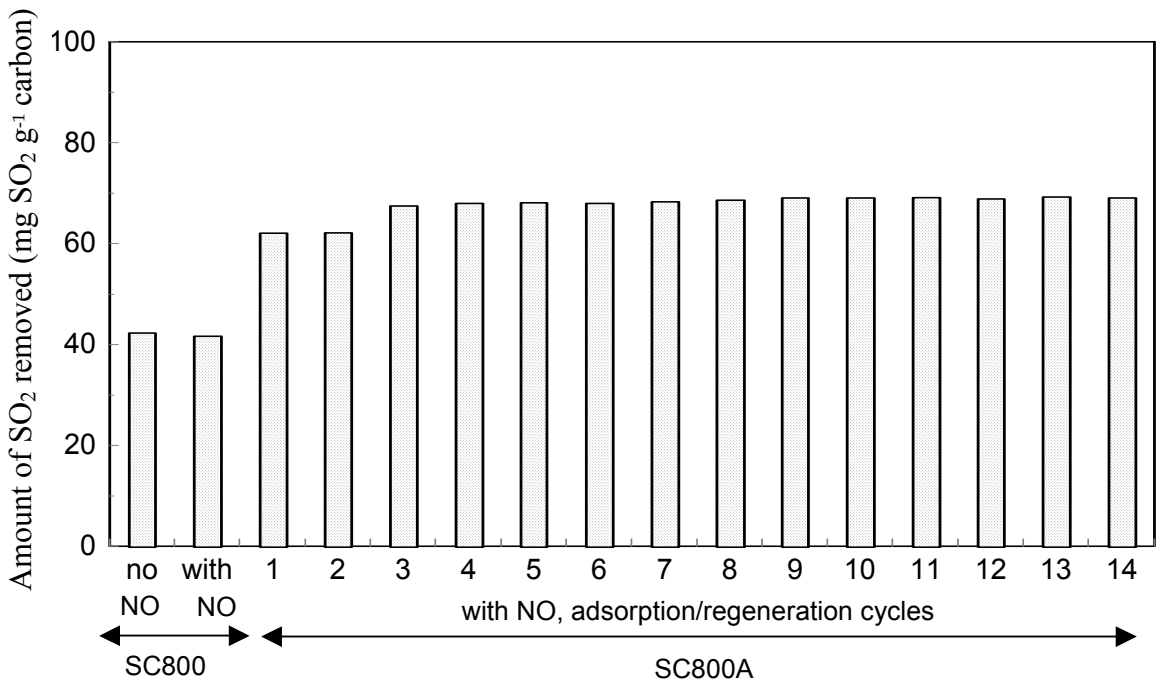
Amount of SO_2 removed (mg SO_2 g^{-1} carbon)
100
80
60
40
20
0
no NO
with NO
1
2
3
4
5
6
7
8
9
10
11
12
13
14
with NO, adsorption/regeneration cycles
SC800
SC800A

Figure 2

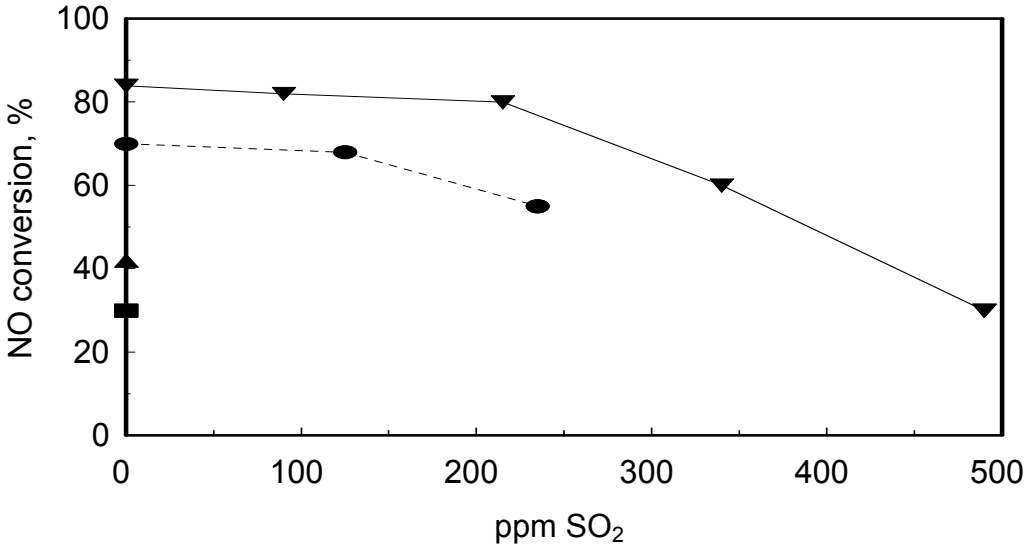

Figure 3